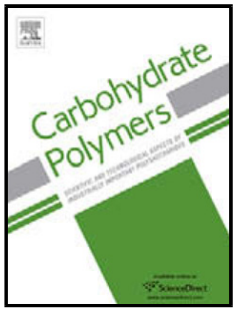

Title: Zinc Chloride Aqueous Solution as a Solvent for Starch

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Highlights:

- ✓ $ZnCl_2$ aqueous solution (>29.6 wt.%) is a non-derivatizing solvent for starch
- ✓ Starch can be dissolved completely and regenerated easily in $ZnCl_2$ solution
- ✓ The suggested dissolution mechanism was the formation of a "zinc-starch complex", not degradation by H^+.

Zinc Chloride Aqueous Solution as a Solvent for Starch

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Abstract:

It is important to obtain starch-based homogeneous systems for starch modification. Regarding this, an important key point is to find cheap, low-cost and low-toxicity solvents to allow complete dissolution of starch and its easy regeneration. This study reveals that a $ZnCl_2$ aqueous solution is a good non-derivatizing solvent for starch at 50 °C, and can completely dissolve starch granules. The possible formation of a "zinc-starch complex" might account for the dissolution; and the degradation of starch, which was caused by the H^+ in$ZnCl_2$ aqueous solution, could not contribute to full dissolution. From polarized light microscopic observation combined with the solution turbidity results, it was found that the lowest $ZnCl_2$ concentration for full dissolution was 29.6 wt.% at 50 °C, with the dissolving time being 4 h. Using Fourier-transform infrared (FTIR), solid state ^{13}C nuclear magnetic resonance(NMR), and X-ray diffraction (XRD), it was revealed that $ZnCl_2$ solution had no chemical reaction with starch glucosides, but only weakened starch hydrogen bonding and converted the crystalline regions to amorphous regions. In addition, as shown by intrinsic viscosity and thermogravimetric analysis (TGA), $ZnCl_2$ solution caused degradation of starch macromolecules, which was more serious with a higher concentration of $ZnCl_2$ solution.

Keywords: starch; $ZnCl_2$ aqueous solution; non-derivatizing solvent; dissolution; zinc-starch complex

Chemical compounds studied in this article:

Starch (PubChem CID: 24836924); Water (PubChem CID: 962); Zinc dichloride (PubChem CID: 5727)

1. Introduction

Starch is one of the most abundant carbohydrates in nature, and has been widely used as a raw material in industry. Furthermore, native starch can be modified into various derivatives to widen its applications. Modified starches such as starch sodium succinate and starch phosphate ester can be used to prepare food additives; and starch can also be converted into value-added chemical products, such as binders and flocculants (Hanselmann & Burchard, 1996; Wu & Hakkarainen, 2014).

However, the modification of starch has been greatly limited by its insolubility in water and most organic solvents. This is especially true if a high degree of substitution (DS) is desired, and in this case modification can only occur in a heterogeneous way. In order to increase the DS, starch esters, for example, were usually prepared in organic solvents, where catalysts may be further added. However, these organic solvents were often volatile, not recyclable, and the catalysts such as pyridine were toxic. These heterogeneous systems have limited the development of starch modification and the application of modified starch (Junistia, Sugih, Manurung, Picchioni, Janssen, & Heeres, 2008).

Homogeneous systems have been reported to be beneficial to carbohydrate modification (Heinze & Liebert, 2011; Gao, Luo, & Luo, 2012). As a result, efforts in recent years have been focused on the search for solvents that can completely dissolve starch. Solvents can be classified into derivatizing and non-derivatizing types according to whether or not any chemical reaction is occurring in the dissolution process. Some traditionally- and broadly-used solvents for starch include dimethyl sulfoxide (DMSO) and strong inorganic alkalis (e.g., KOH and NaOH). However, research has shown that alkaline solutions may induce undesirable side reactions such

as structural depolymerization and oxidation (Jackson, Choto-Owen, & Waniska, Rooney, 1988; Jordan, Schmidt, Liebert, & Heinze, 2014). DMSO was found to be able to dissolve starch without structural degradation (Everett & Foster, 1959). However, the dissolution process with DMSO is not straight forward. Starch is heated in 90% aqueous DMSO for about 24 h, followed by precipitation and re-dissolution in water (with further heating); and this procedure requires intensive shear and thermal treatment to starch (Chakraborty, Sahoo, Teraoka, & Gross, 2005; Han & Lim, 2004; Zhong, Yokoyama, Wang, & Shoemaker, 2006).

Ionic liquids (IL's) represent a new class of solvents for starch, which have gained much attention recently. IL's have been claimed as "green solvents" for many substances including natural polymers such as starch and cellulose, because of their chemical and thermal stability, low vapor pressure, and high ionic activity (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Lu, Yan, & Texter, 2009). However, the research on IL's has just been started and the toxicity of IL's remains uncertain. Jastorff et al. and Matsumoto et al. (Jastorff et al., 2003; Matsumoto, Mochiduki, Fukunishi, & Kondo, 2004) have preliminarily studied the toxicity of IL's and proved that the commonly-accepted notion that IL's have low toxicity is incorrect. Most IL's are designed with large organic cations, such as pyridinium, imidazolium and pyrrolidinium while the anions are hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), dicyanamide ($N(CN)_2^-$), etc.. Their release to aquatic environments could cause severe water and soil contamination due to the potential toxicity and non-biodegradability (Gathergood & Scammells, 2002). Moreover, the high prices of IL's make them difficult to be applied practically in industry. Therefore, the practical application of IL's remains uncertain.

Another class of solvents for natural polymers is inorganic salt hydrates, which

are liquids that have a designated water-salt mole ratio close to the coordination number of the strongest hydrated ion. Typical examples are liquid phases of solid salt hydrates, such as $Ca(SCN)_2/H_2O$ (Warwicker, Jeffries, Colbran, & Robinson, 1966), $LiSCN/H_2O$ (Lukanoff, Schleicher, & Philipp, 1983) and $ZnCl_2/H_2O$ (Letters, 1932). They are inexpensive, convenient, and environmentally friendly. They are non-derivatizing solvents not only being regarded as very efficient solvents for most natural polymers such as cellulose (Cao, Xu, Chen, Gong, & Chen, 1994), chitin (Wang, Pedersen, Deng, Qiao, & Hou, 2013), but also have been applied as a medium for the chemical functionalization or derivatization, such as carboxymethylation and esterification, of these natural polymers, within a short reaction time (Leipner, Fischer, Brendler, & Voigt, 2000; Sen, Martin, & Argyropoulos, 2013). For example, Heinze et al. used molten $LiClO_4/3H_2O$ as a solvent for homogeneous carboxymethylation of cellulose with a high DS (i.e., <2) in a one-step synthesis after a short reaction time of 4 h (Fischer, Thümmler, Pfeiffer, Liebert, & Heinze, 2002). Acetylation could also be carried out at a temperature of 130 °C for a short reaction time (0.5-3.0 h) with DS between 1 and 2.5 (Fischer, Leipner, Thümmler, Brendler, & Peters, 2003). When cellulose is dissolved in a molten salt hydrate, the formation of a homogeneous phase makes cellulose hydroxyl groups completely available for chemical derivatization. This allows the control of both the degree of substitution and the distribution of functional groups, which can undoubtedly broaden the reaction paths and the diversity of products. However, there has been no report on molten salt hydrates applied as solvents or reaction media for starch.

Thus, the aim of the present work was to investigate the ability of $ZnCl_2$ aqueous solution, a molten salt hydrate, as a solvent for starch, together with the structure and properties of the regenerated starch from this solvent.

2. Materials and Methods

2.1. Materials

Native cassava starch (with moisture content of 14%) was obtained from Dongguan Wenying Starch Trade Co., Ltd., without further treatment. Anhydrous zinc chloride ($ZnCl_2$) and methanol (analytical grade) were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). Other chemicals including hydrazine sulfate and hexamethylenetetramine were of analytical grade and used as received without further purification. All solutions were prepared with distilled water.

2.2. Dissolution and regeneration of starch from zinc chloride solutions

Certain amounts of anhydrous $ZnCl_2$ were added to a three-neck, round-bottom flask equipped with an electric stirrer to obtain $ZnCl_2$ aqueous solutions of certain concentrations (65%, 43%, 35% and 29.6%). The $ZnCl_2$ solution was then mixed with a certain amount of starch (2.0 wt.%, dry weight). Then, the system was stirred at 50 °C for 4 h. In order to prevent degradation by shear force, the revolution speed was set as 60 rpm. Besides, during the dissolution process, the solution was sampled at intervals and observed under a polarized light microscope (Motic BA300POL, Motic Asia, Hongkong) equipped with a digital camera (Moticam Pro 205A, Motic Asia, Hongkong).

Regenerated starch was obtained from the above solutions by adding absolute ethanol with continuous stirring (The absolute ethanol was about 2-5 times the volume of the starch solution). The starch samples were then dried and smashed into powder for further analysis.

$ZnCl_2$ aqueous solution was acidic (pH = 4.09 for 29.6% and pH = 0.67 for 65%).

For discussing the influence of H^+ on starch, hydrochloric acid (HCl) solution with a pH value of 4.09 was prepared. After that, native cassava starch was treated with the HCl solution under the exactly same processes as with $ZnCl_2$ aqueous solution. And regenerated starch from HCl solution was collected and compared with those from $ZnCl_2$ aqueous solution.

2.3. Characterization of starch and regenerated starch

Fourier-transform infrared (FTIR) spectra for native and regenerated starches were obtained in the range of 400–4000 cm^{-1} with a TENSOR27 FTIR model manufactured by Burker, Germany. The samples were mixed with KBr and well ground before being pressed into wafers.

X-ray diffraction (XRD) patterns for native and regenerated starches were obtained on an PW3040/60 X'pert PRO X-ray diffractometer (PANalytical, Netherlands) using the Cu-Ka X-ray source operating at 36 kV and 20 mA. The scanning range and rate are 5–90° and 4°/min, respectively.

Solid-state ^{13}C CP/MAS spectra were collected on a Bruker Avance 500 nuclear magnetic resonance (NMR) spectrometer using a 4mm MAS BB-1H probe head. The spectral width used was 37.6 KHz. The acquisition time was 27 ms, together with 7.7 μs pre-scan delay and 13.3 μs dwell time. All solid experiments were carried out at 125.8 MHz for ^{13}C with 4096 scans accumulating for each spectrum.

To determine the intrinsic viscosity of native and regenerated starches (Islam, Mohd, & Noor, 2001), the samples were dispersed in 0.5mol/L KOH solutions and stirred in a boiling water bath for 10 min. The solutions were then cooled to room temperature and left overnight. The final concentrations of the solutions were 2.6–6.0 mg/mL. Intrinsic viscosity measurements were obtained using a Ubbelohde

dilution capillary viscometer (size 37, Shanghai Liangjing Glass Instrument Factory, China) immersed in a water bath maintained at 25±0.1 °C. The efflux time of solvent and solutions were measured in triplicate and averaged. Results were expressed as relative viscosity (η_r), $\eta_r=\eta/\eta_0$; specific viscosity (η_{sp}), $\eta_{sp}=\eta_r-1$; and intrinsic viscosity ([η]). η is the solution viscosity and η_0 is the solvent viscosity. Intrinsic viscosity, [η], was then calculated as the zero concentration-limit of the η_{sp}/c value resulting from the plots of η_{sp}/c versus c straight lines (c represents the concentration of solvent).

The thermal decomposition of native and regenerated starches was determined by a thermogravimetric analysis (TGA) apparatus (TGA4000, PerkinElmer, USA) in an open system (Liu, Yu, Liu, Chen, & Li, 2009). Starch samples were heated to 800 °C at 20 °C/min. The weight loss results were also converted to derivative weight percentages to measure and compare the peak temperatures. The temperature calibration was done by the Curie temperatures of nickel and iron.

3. Results and discussion

3.1. Solubility of starch in $ZnCl_2$ aqueous solutions

Fig. 1 showed the photos of cassava starch (2% concentration) dispersed in $ZnCl_2$ aqueous solution (29.6 wt.%). Starch was seen to be fully dissolved in the solution, as a clear and transparent solution was formed without any sediment (Fig. 1a). In contrast, when starch was dispersed in water, it was only suspended and the solution was turbid (Fig. 1b). In this case, starch granules could only partially swell in water without gelatinization, as the temperature was 50 °C which is lower than the gelatinization temperature of cassava starch.

Since $ZnCl_2$ aqueous solution was acidic (pH 4.09 at 29.6% concentration), it is necessary to discuss the influence of H^+ on starch. Fig. 1c shows that when starch was dispersed in a HCl solution (pH 4.09), the granules were also suspended in the solvent and no transparent solution could be obtained.

The effect of H^+ on starch granules has been studied since 1885 (Lintner, 1886), and different modified starch products can be produced based on it. Lintnerized starch was the first water soluble starch which was prepared by treatment of starch in 7.5% (w/v) HCl for one week at 22-24 °C, or for three days at 40 °C. Nowadays, commercial soluble starch is still produced by this old procedure (Johnston, Mukerjea, & Robyt, 2011). Besides, microporous starch can also be prepared by treatment of starch in acid solution (Kimura & Robyt, 1995).

While the degradation of starch is inevitable with H^+ in the solution, the process progresses from the amorphous region to the crystalline region (Srichuwong, Isono, Mishima, & Hisamatsu, 2005; Chen, Yu, Simon, Liu, Dean, & Chen, 2011). Specifically, due to the small molecular size, H^+ can penetrate into the pores on the granule surface, which are the radial channels into the granule interior. Since the amorphous region is looser than the crystalline region, H^+ preferably attacks the amorphous region, with the crystalline region being mostly intact. Therefore, the starch granules can only form a classic “Swiss cheese” appearance in acidic solution, and cannot completely be dissolved. In other words, the degradation of starch granules by H^+ can only result in a suspension (as shown inFig. 1c). Therefore, although $ZnCl_2$ aqueous solution is acidic, the mechanism for dissolution of starch granules should not be based on the H^+ in the solution.

Fig. 2 showed the birefringence (Maltese crosses) changes of cassava starch granules during dissolution in 29.6% $ZnCl_2$ aqueous solution. It could be seen that the

starch granules exhibited clear birefringence initially after mixing (Fig. 2a). Then, with the elapse of time, the amount and size of birefringence was observed to decrease (Fig. 2b~2d). After an even longer time (4 h), the visual field gradually turned dark, and all birefringence disappeared totally (Fig. 2d), suggesting that starch granules dissolved completely. Thus, for 2% cassava starch in 29.6% $ZnCl_2$ aqueous solutionat 50 °C, the dissolution time was 4 h.

As is known, the main ions in $ZnCl_2$ aqueous solution are H^+, Zn^{2+} and Cl^-. Since starch is slightly acidic in nature and is negatively charged, Cl^- is repelled by starch molecules (Oosten, 1990). H^+ attacked the amorphous region initially, which only resulted in partial degradation of starch granules, but not dissolution. Thus, it was highly possible that the interaction between Zn^{2+} and starch molecules led to the dissolution. Cao et al. (Cao, Xu, Chen, Gong, & Chen, 1994) proved the presence of a zinc-cellulose complex after microcrystalline cellulose (Avicel) was treated with $ZnCl_2$ aqueous solution. Since starch has the same monosaccharide (glucose) and intermolecular force between molecules (hydrogen bonding) as cellulose, a similar complex may be formed between Zn^{2+} and starch molecules. Furthermore, Islam et al. (Islam, Mohd, & Noor, 2001) found that when starch is added to sodium chloride solution, sodium ions penetrate into starch chains, replacing H^+ which migrates to the water phase; as a result, “sodium salts of starch” are formed. Here in this study, it was possible that a “zinc-starch complex” was formed. Specifically, Zn^{2+} can penetrate into the inner structure of starch, weakening the intra- and inter-molecular hydrogen bonds, disrupting the crystalline region, and forming a “zinc-starch complex” with starch chains. This could be the dominant factor for starch dissolution in $ZnCl_2$ aqueous solution.Regarding this complexity, further research is required.

Turbidity was also used to determine the dissolution of starch in aqueous $ZnCl_2$

238 solution as it represents the cloudiness of a fluid caused by particles in suspension.
239 Turbidity is expected to keep reasonably constant as long as the solute is perfectly
240 soluble, but it will increase sharply with newly added solute remaining solid when the
241 maximum solubility is reached (Mazza, Catana, Garcia, & Cecutti, 2009). As shown
242 in Fig. 3, the starch (2 wt.%) was totally dissolved in 65% $ZnCl_2$ aqueous solution and
243 formed a clear and transparent solution without any sediment. The turbidity in this
244 case was low (about 21.9 NTU). When the $ZnCl_2$ concentration was decreased, the
245 turbidity increased very moderately. Nevertheless, when the $ZnCl_2$ concentration was
246 below 29.6%, precipitation started to appear and the turbidity increased sharply. This
247 suggests that the $ZnCl_2$ concentration needs to be ≥29.6 wt.% for full dissolution of
248 starch (2 wt.%).
249
250 *3.2. FTIR spectra fornative and regenerated starches*
251 The FTIR spectra of native cassava starch and regenerated starch from 29.6%
252 $ZnCl_2$ aqueous solution were shown in Fig. 4. The spectra of regenerated starch were
253 quite similar to the native counterpart and no new characteristic peaks were found,
254 indicating no chemical changes to the glucosides in the regenerated starch. Thus, the
255 $ZnCl_2$ aqueous solution can be considered as a non-derivatizing solvent for starch.
256 Nevertheless, there were also some differences in band wave numbers between
257 native and regenerated starches. As seen from Fig. 4, the O-H bending of adsorbed
258 water at 1647 cm^{-1} was shifted to 1627 cm^{-1}, indicating that the water absorption
259 function of regenerated starch became worse (Vicentini, Dupuy, Leitzelman, Cereda,
260 & Sobral, 2005). Moreover, in the adsorption band between 1100 cm^{-1} and 900 cm^{-1},
261 which indicates the interactions of hydrogen bonds, the peak at 1016 cm^{-1} was shifted
262 to 1020 cm^{-1} and the one at 929 cm^{-1} was shifted to 935 cm^{-1}. According to Ahmad et

al. and Ma et al. (Ahmad, Anuar, & Yusof, 2011; Ma, Yu, & Zhao, 2006), the peak at the low wave number results from the strong hydrogen bonds that drag the relative groups to a lower vibration frequency, and the peaks at the higher wave number are due to the weak interaction of hydrogen bonding. Thus, the above changes in wave numbers indicated less hydrogen bonding in regenerated starch.

All in all, aqueous $ZnCl_2$ could be considered as a non-derivatizing solvent for starch without causing obvious change to the starch glucosidic structure but can destroy the inter- and intra-molecular hydrogen bonding in starch.

3.3. Solid state ^{13}C NMR study of native and regenerated starches

For further understanding the effects of $ZnCl_2$aqueous solution on starch, ^{13}C NMR spectra on native cassava starch and regenerated starch were obtained (Fig. 5). It can be seen that both native and regenerated starches showed very similar spectra which had four dominant NMR signals. The signals at 90–110 ppm and 81–85 ppm were attributed to C-1 and C-4, respectively, while the signal at 59–65 ppm was assigned to hydroxymethyl C-6. The large signal around 70–79 ppm was associated with C-2, C-3, and C-5 (Morrison, Tester, Gidley, & Karkalas, 1993). Except these, no new peaks appeared in the regenerated starch ^{13}C NMR spectrum.

Compared with the spectra for native and regenerated starch, two distinct differences could be observed: the chemical shifts of C-1 peak (from 103.66 ppm to 105.18 ppm), and the increase inintensity of C-4 peak. The sharp signal intensity of C-4 peak showed an increase in amorphous content (Atichokudomchai, Varavinit, & Chinachoti, 2004; Fan et al., 2013), suggesting that $ZnCl_2$ aqueous solution destroyed the crystalline region and changed it into amorphous starch. And the shifts of C-1 peak could result from the interaction between Zn^{2+} and hydroxyl groups to form a

288 complex (Cao, Xu, Chen, Gong, & Chen, 1994). This complex could be the
289 "zinc-starch complex" as mentioned before.
290
291 *3.4. XRD analysis of native and regenerated starches*
292 Native cassava starch and regenerated starch after treatment with $ZnCl_2$ aqueous
293 solutions of different concentrations were examined by XRD, and the results were
294 shown in Fig. 6. Native starch exhibited a typical A-type XRD pattern, giving strong
295 reflections at about 15°, 23° and unresolved doublet at nearly 17° and 18°(2θ)
296 (Cheetham & Tao, 1998; Kuo & Lai, 2007). In contrast, the regenerated starch only
297 had a dispersive broad peak and showed no crystalline peaks. This suggested that the
298 crystalline region of native starch was completely damaged during the dissolution.
299 The loss of crystallinity could be attributed the penetration into starch of Zn^{2+} which
300 weakened the inter- and intra- molecular hydrogen bonds of starch (Gao, Luo, & Luo,
301 2012). These results were in agreement with the shifts in the FTIR and NMR signals.
302
303 *3.5. Intrinsic viscosity analysis ofnative starch and regenerated starch*
304 Polymer intrinsic viscosity, [η], is an important parameter reflecting the size of a
305 macromolecule in a given solvent at a certain temperature (Liu & Budtova, 2013).
306 This parameter is determined using the classical Huggins equation (see the Materials
307 and Methods section). Fig. 7 shows the intrinsic viscosity of native starch and
308 regenerated starch. Native starch was observed to exhibit the highest intrinsic
309 viscosity (about 192 mL/g). With the increased concentration of $ZnCl_2$aqueous
310 solution, the intrinsic viscosity of regenerated starch apparently decreased, from
311 158 mL/g for 29.6% $ZnCl_2$ aqueous solution, to 126 mL/g for 65% $ZnCl_2$ solution.
312 The intrinsic viscosity of polymers is caused by the friction force between the

313 solvent and the solute in dilute solution, and can be used to reflect the size of the
314 macromolecular conformation in the certain solution (Wolf, 2007). For starch, no
315 matter amylopectin or amylose, the size of their macromolecular conformation was
316 caused by the degree of polymerization (DP), namely the molecular weight of
317 macromolecules (Higiro, Herald, Alavi, & Bean, 2007). Therefore, from the
318 decreased intrinsic viscosity, it can be deduced that the starch dissolution in $ZnCl_2$
319 aqueous solution was accompanied by the degradation of starch chains, which mainly
320 resulted from the attack by H^+. Since $ZnCl_2$ aqueous solution of higher concentration
321 had lower pH, the intrinsic viscosity of regenerated starch decreased correspondingly.
322 Moreover, Fig. 7 also shows the intrinsic viscosity of regenerated starch from a
323 HCl solution (pH 4.09), which was apparently lower than that of regenerated starch
324 from 29.6% $ZnCl_2$aqueous solution (pH 4.09). It was possible that the "zinc-starch
325 complex" prevented starch chains from being attacked by H^+. Nonetheless, this needs
326 further studies. Also, the accurate quantitative relationship between $ZnCl_2$ solution
327 concentration and starch molecular weight will be discussed in our ongoing research.
328
329 *3.6. Thermal decomposition of native and regenerated starches*
330 Based on previous research, the thermal decomposition temperature of starch
331 without chemical modification is mainly based on the DP of starch molecular chains,
332 and is not significantly influenced by its crystallinity or granule size (Liu et al., 2013).
333 The derivative weight percentage of starch samples (DTG) could be seen in
334 Fig. 8. There were two peaks on the DTG curves. The first one represented moisture
335 evaporation, which occurred with the increased temperature until ca.110 °C. The
336 percentage of weight loss in this step was dependent on the moisture content in starch.
337 The second weight loss peak corresponded to the thermal decomposition of starch

molecular chains. For native starch, this peak located at 337 °C. For regenerated starch from 35%, 43% and 65% $ZnCl_2$ solutions, this peak located at 271 °C, 253 °C and 250 °C, respectively. The decomposition temperature of native starch was significantly higher than those of regenerated starch, indicating the reduction in DP of starch molecular chains after dissolution in $ZnCl_2$ solutions. Moreover, the decomposition temperature of regenerated starch was decreased with the increased concentration of $ZnCl_2$ solution, also showing that a higher concentration of $ZnCl_2$ solution caused greater degradation of starch macromolecules. These results are in agreement with the intrinsic viscosity results.

4. Conclusions

$ZnCl_2$ aqueous solution can be used as an effective solvent for starch at 50 °C, which is inexpensive and environmentally friendly. For 2 wt.% starch, the lowest $ZnCl_2$ concentration to allow full dissolution of starch was 29.6 wt.%, with the dissolving time being 4 h. By characterizing the structure and properties of regenerated starch, $ZnCl_2$ aqueous solution was found to be a non-derivatizing solvent for starch without causing changes to starch glucosidic structure, but only destroying the inter- and intra- molecular hydrogen bonds of starch and converting the crystalline structure to amorphous state. This is albeit the inevitable degradation of starch chains since $ZnCl_2$ aqueous solution was acidic. The partial degradation by acid could not be the mechanism of dissolution as it acted mostly to the amorphous region of starch granules. Instead, the dissolution was more likely to rely on the formation of a "zinc-starch complex".

Further research will be focused on the dissolution mechanism including the verification of the proposed "zinc-starch complex". Besides, it is worth to study the

interactions between starch and other salt hydrates, the accurate quantitative relationship between $ZnCl_2$ solution concentration and starch molecular weight, and the chemical modification of starch in a homogeneous phase with $ZnCl_2$ aqueous solution as a reaction medium.

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508

Figure Captions

Fig. 1. Pictures of cassava starch (2% concentration) dissolved in 29.6% $ZnCl_2$ aqueous solution (a), water (b) and HCl solution (c) after stirring for 4 h

Fig. 2. Birefringence images for 2% cassava starch granules dissolved in 29.6% $ZnCl_2$ aqueous solution for 0 h (a), 1 h (b), 2 h (c), 3 h (d), and 4 h (e)

Fig. 3. Turbidity of starch dissolved in aqueous$ZnCl_2$ of different concentrations

Fig. 4. FTIR spectra for native cassava starch (a) and regenerated starch from 29.6% $ZnCl_2$ aqueous solution (b)

Fig. 5. ^{13}C NMR spectra for native starch and regenerated starch from 29.6% $ZnCl_2$ aqueous solution

Fig. 6. XRD patterns for regenerated starch samples from 35% (a), 43% (b), 65% (c) $ZnCl_2$ solutions, and native starch (d)

Fig. 7. Intrinsic viscosity of native starch (a), and regenerated starch from 29.6% (b), 43% (c), 65% (d) $ZnCl_2$ solutions, and from HCl solution (pH=4.09) (e)

Fig. 8. TGA results for native starch (A), and regenerated starch samples from 35% (B), 43% (C) and 65% (D) $ZnCl_2$ solution.

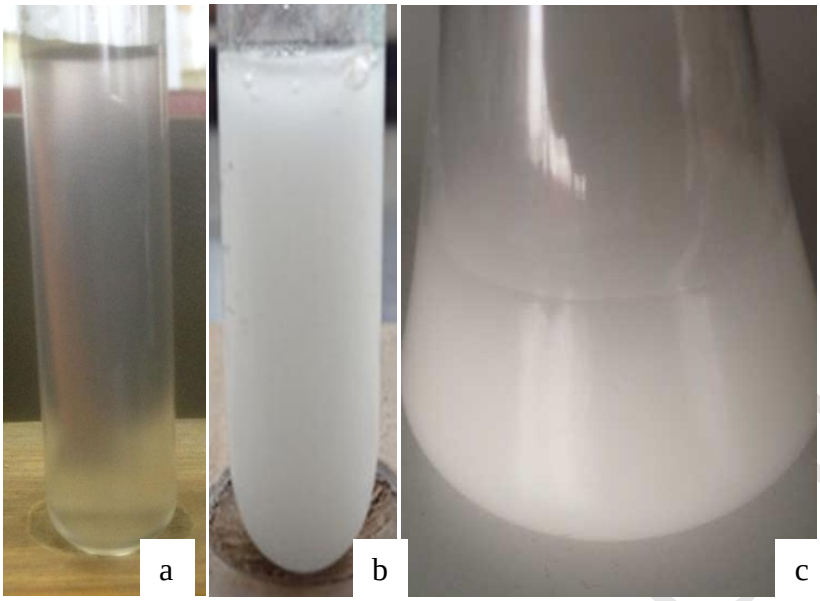


Fig. 1. Pictures of cassava starch (2% concentration) dissolved in 29.6% $ZnCl_2$ aqueous solution (a), water (b) and HCl solution (c) after stirring for 4 h.

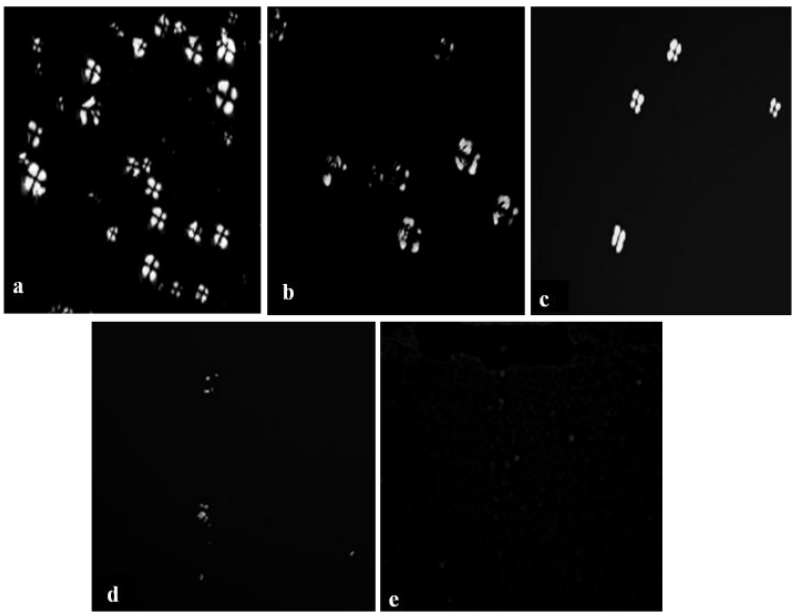


Fig. 2. Birefringence images for 2% cassava starch granules dissolved in 29.6% $ZnCl_2$ aqueous solution for 0 h (a), 1 h(b), 2 h(c), 3 h(d), and 4 h(e).

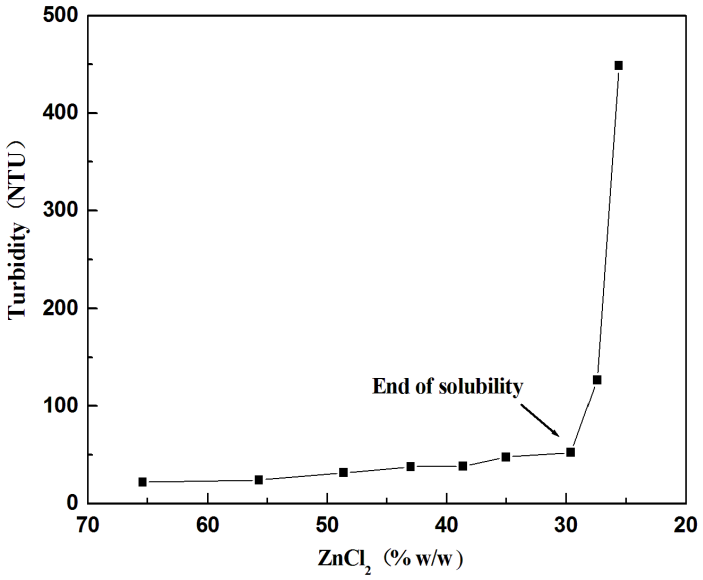


Fig. 3. Turbidity of starch dissolved in aqueous $ZnCl_2$ of different concentrations.

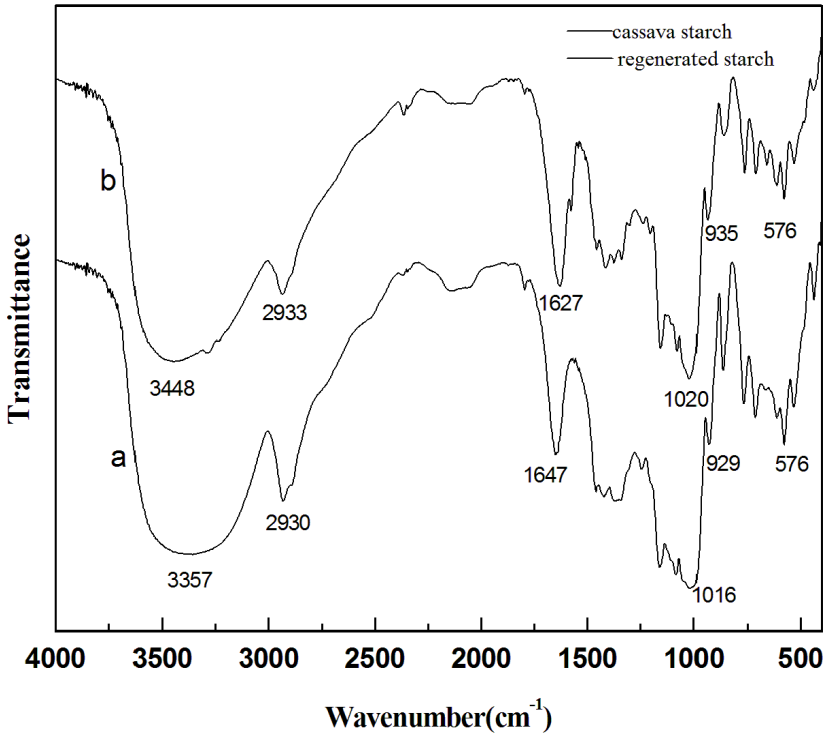


Fig. 4. FTIR spectra for native cassava starch (a) and regenerated starch from 29.6% $ZnCl_2$ aqueous solution (b).

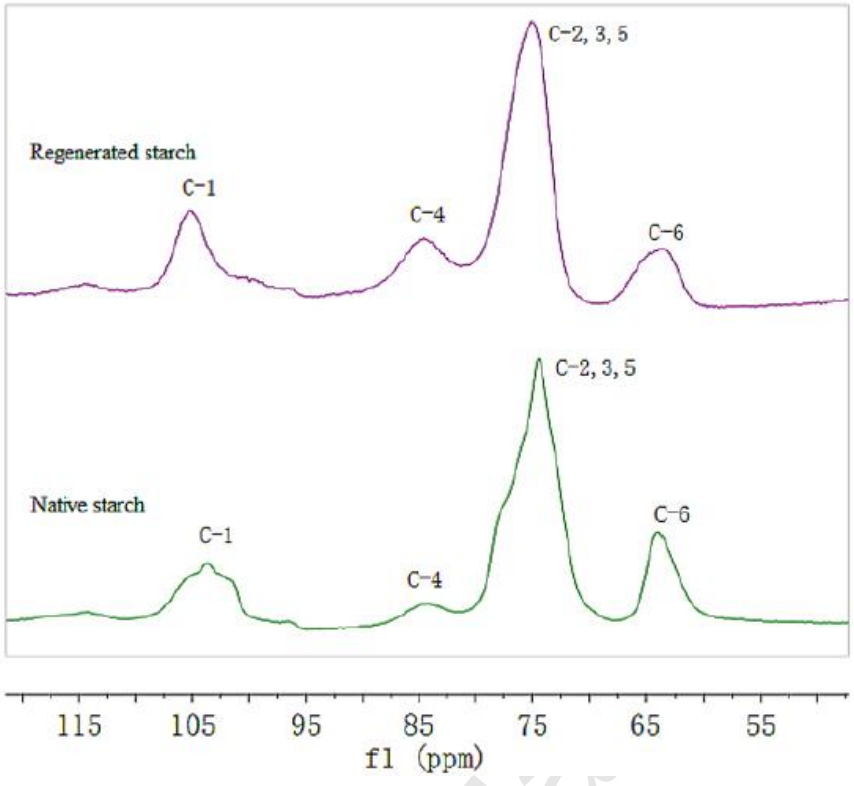


Fig. 5. ^{13}C NMR spectra for native starch and regenerated starch from 29.6% $ZnCl_2$ aqueous solution.

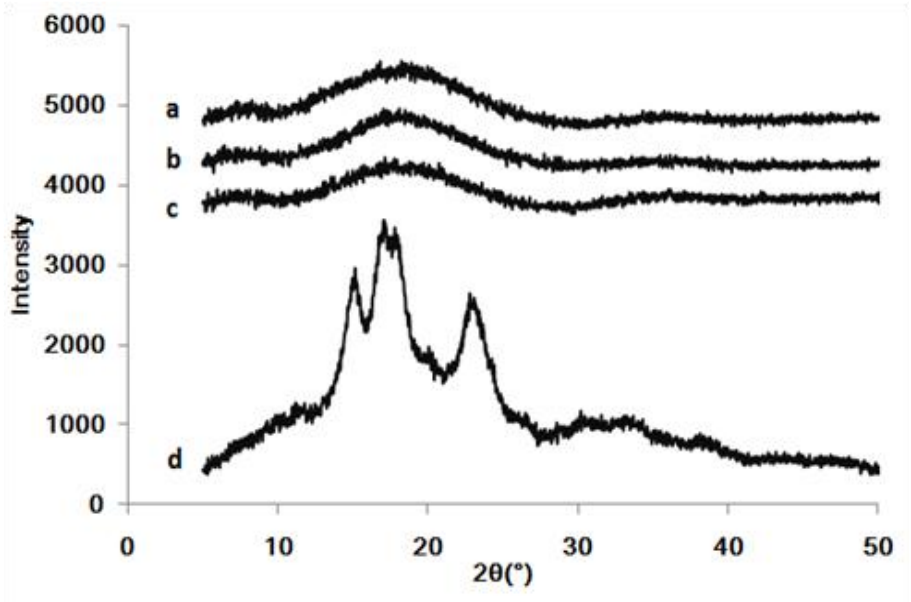
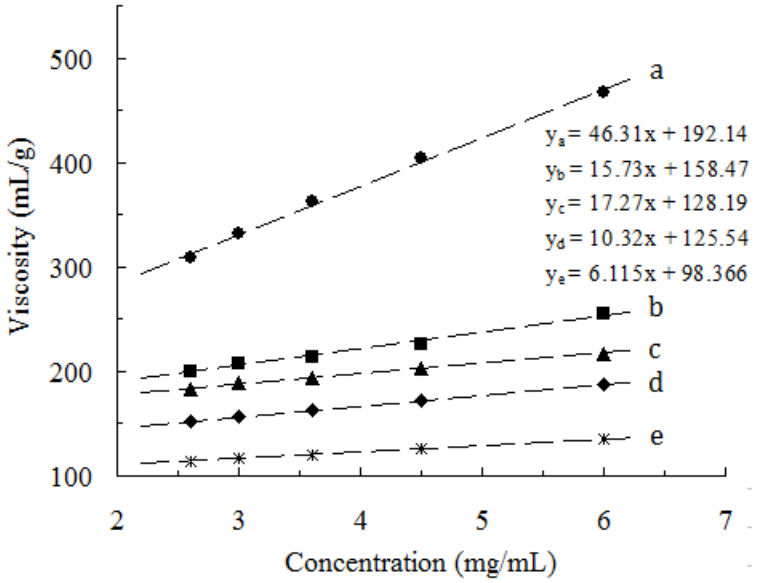


Fig. 6. XRD patterns for regenerated starch samples from 35% (a), 43%(b), and 65%(c) $ZnCl_2$ solutions, and native starch (d).



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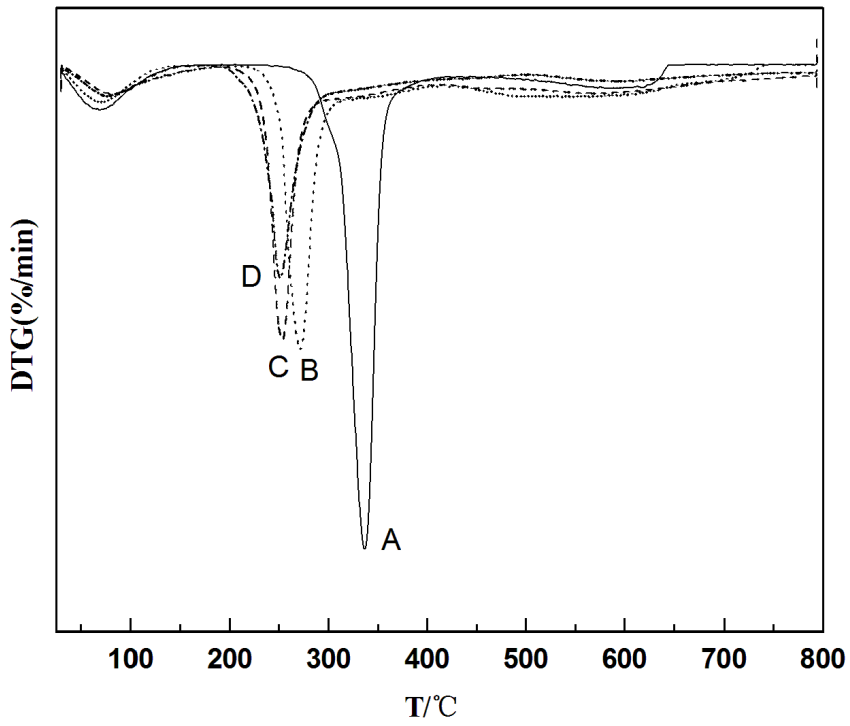

Fig. 8. TGA results for native starch (A), and regenerated starch samples from 35%(B), 43%(C) and 65% (D)$ZnCl_2$ solution.